

University of Groningen

Investigation of molecular dimers by ensemble and single molecule spectroscopy

Christ, Th.; Petzke, F.; Bordat, P.; Herrmann, A.; Reuther, E.; Müllen, K.; Basché, Th.

Published in:
Journal of Luminescence

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2002

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Christ, T., Petzke, F., Bordat, P., Herrmann, A., Reuther, E., Müllen, K., & Basché, T. (2002). Investigation of molecular dimers by ensemble and single molecule spectroscopy. *Journal of Luminescence*, 98, 23-33.

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.



ELSEVIER

Journal of Luminescence 98 (2002) 23–33

JOURNAL OF
LUMINESCENCE

www.elsevier.com/locate/jlumin

Investigation of molecular dimers by ensemble and single molecule spectroscopy

Th. Christ^a, F. Petzke^a, P. Bordat^b, A. Herrmann^b, E. Reuther^b,
K. Müllen^b, Th. Basché^{a,*}

^a *Institut für Physikalische Chemie, Johannes Gutenberg-Universität, Welderweg 11, D 55099 Mainz, Germany*

^b *Max-Planck-Institut für Polymerforschung, 55128 Mainz, Germany*

Abstract

We have investigated molecular dimers with different electronic coupling strengths by bulk and single molecule spectroscopy. In one of the dimers the two monomers (perylene-monoimide) are directly connected via a single bond while in the other one they are separated by the benzil motif. The close proximity of the monomers in the first case gives rise to excitonic band splitting which is clearly observable in the bulk absorption spectra. For the benzil structure the electronic interactions are governed by Förster-type energy hopping between the monomers. Fluorescence intensity trajectories at the single molecule level show one-step and two-step bleaching behaviour which appears to be very similar for both dimers. However, emission spectra recorded simultaneously with the trajectories indicate spectral changes which allow to distinguish between weakly and strongly coupled dimers. In the latter case the spectral shape changes significantly when excitonic coupling has been lifted because of photochemical transformation of one of the monomers. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Single molecule spectroscopy; Electronic interactions; Excitons; Molecular aggregates

1. Introduction

The optical properties of molecular aggregates or multichromophoric assemblies are typically influenced by electronic interactions among the chromophores. The strength of these interactions depends on the distance and relative orientation of the chromophoric units and the magnitude of their electronic transition dipoles. Assuming negligible interchromophore electron overlap and electron exchange, two regimes of interactions are of

primary interest. When the chromophores are in close proximity the interaction between the transition dipoles will give rise to excitonic states which may be delocalised over the whole aggregate [1,2]. Such systems are characterised by collective optical properties which may become visible in appreciable shifts of the absorption and emission lines. Well-known examples are the famous J-aggregates which show a strong red-shift in absorption [3,4]. At intermolecular distances where excitonic splittings can be neglected, incoherent electronic energy transfer between the chromophores can occur. This is the regime of fluorescence resonance energy transfer (FRET) which can be described by Förster type

*Corresponding author. Tel.: +49-6131-3922-707; fax: +49-6131-3923-953.

E-mail address: thomas.basche@uni-mainz.de (Th. Basché).

dipole–dipole interaction [1,5]. Unidirectional FRET between a donor and an acceptor moiety is a valuable tool to measure distances and distance fluctuations at a length scale of several nanometers [6]. It is obvious that the transition between excitonic interactions and FRET is not sharp.

Recently, various kinds of multichromophoric assemblies like conjugated polymer molecules [7], light-harvesting pigments [8–11], donor–acceptor substituted biopolymers [12,13] or dendrimers carrying different numbers of chromophores [14,15] have been studied by single molecule spectroscopy. A strong motivation for these experiments relates to the fact that electronic interactions can then be studied without averaging over the properties of an intrinsically inhomogeneous ensemble. Actually, the results obtained so far have revealed a number of novel phenomena. To name just a few, fluorescence intensity fluctuations of single conjugated polymer molecules could be attributed to localised quenching defects along the polymer chain [7] and low-temperature studies of light harvesting pigments have improved our understanding of excitation delocalisation in photosynthetic assemblies [10]. Interestingly, most of the studies of single multichromophoric assemblies point to common features, although the chemical structures of the chromophores might be vastly different. One prominent example is the observation of complete emission quenching by a single photo-induced trap state.

A complication inherent to the study of multichromophoric systems is to sort out phenomena, which might originate from differences in coupling strengths between the chromophores caused by variations of inter-chromophore distances. To mediate this problem, we have started experiments with the simplest type of molecular aggregates, i.e. molecular dimers. In particular, we have investigated two dimers in which the identical monomer units—perylene monoimides—are covalently held together at different distances giving rise to a variation of coupling strengths. Perylene-carboximides are quite stable chromophores which recently have been covalently assembled to various kinds of multichromophoric aggregates [14,16]. In the present work, we have studied Perylenemono-

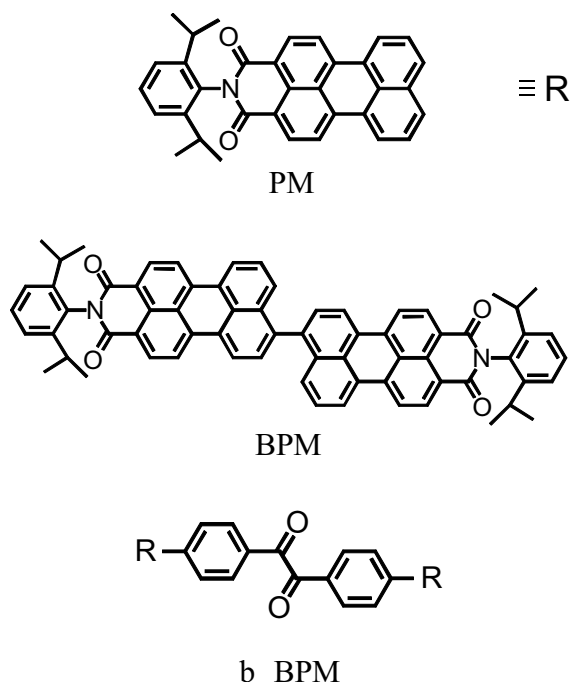


Fig. 1. Chemical structures of the compounds investigated: Perylene-monoimide (PM), Bi-Perylene-monoimide (BPM) and two PM molecules interconnected by the benzil motif (b_BPM). Please note that neither BPM nor b_BPM are planar structures.

imide (PM), Bi-Perylenemonoimide (BPM) and benzilic Bi-Perylenemonoimide (b_BPM: two Perylenemonoimides connected by the benzil motif). The chemical structures of the monomer and both dimers are presented in Fig. 1. The differences in electronic interaction strengths between BPM and b_BPM already show up in the bulk solution absorption and emission spectra. Related information about the coupling strength or alterations of it are obtained by analysing spectral shifts and fluorescence intensity changes observed at the single molecule level.

2. Experimental

Absorption spectra of PM, BPM and b_BPM in tetradecane were measured on an Omega 20 spectrometer (Bruins Instruments). Fluorescence

spectra of the same systems were recorded with a FluoroMax2 fluorometer (JobinYvon-Spex).

Samples for the single molecule experiments were prepared by spin-coating solutions of PM, BPM and b_BPM (5×10^{-10} mol/l) in toluene containing 6 g/l zeonex (a polycyclo-olefine polymer) on a glass cover slide at 3000 rpm to yield thin (around 30 nm) polymer films.

The single molecule experiments were performed with a confocal microscope built on a Zeiss Axiovert 135 TV system. The microscope has been described in detail elsewhere [17]. In brief, an argon/krypton mixed gas laser (Innova 70-Spectrum, Coherent) was used for excitation of the dye molecules at 488.0 nm. After suppression of residual plasma lines by a laser line filter and variable attenuation, the expanded laser beam was guided into a high-numerical-aperture microscope objective (NA=0.9, Zeiss) by reflection from a dichroic mirror (FT 510 or FT 505). The polymer film samples were mounted on a piezo scanner (PI), allowing x – y translation of the specimen. The microscope objective served to both focus the laser beam onto the sample and collect the emitted fluorescence and scattered excitation light from the nearly diffraction-limited sample volume. The Stokes-shifted fluorescence passed a dichroic mirror and was focused by a tube lens onto a detection pinhole (80 μ m) for spatial filtering. A 488 holographic notch filter (Kaiser Optical Systems) was used for further suppression of residual laser light. The remaining light was divided by a 50:50 beam-splitter and focused onto an avalanche photodiode (AQR 14, EG&G) and the entrance slit of a spectrograph (Spectra Pro 500, Acton Research Cooperation) equipped with a LN₂ cooled CCD camera (LN/1100 PB, Roper Scientific). This set-up allowed the simultaneous recording of the fluorescence intensity as a function of time (fluorescence time traces) and fluorescence emission spectra.

The overall detection efficiency of our set-up was $\sim 5\%$. Typically, a sample area of about $10 \times 10 \mu\text{m}^2$ was scanned through the focus of the microscope objective and the total fluorescence intensity was recorded as a function of the x – y position. In a suitably diluted sample the diffraction limited spots corresponding to single dye

molecules could then easily be discerned. Keeping the piezo scanner positioned stationary on one of these spots allowed recording of single-molecule dispersed fluorescence spectra or fluorescence time-traces. The spectra were measured with an integration time of 5 s and the time-traces with dwell times of 50 or 100 ms. The excitation intensity was typically set to 4.4 kW/cm^2 .

3. Absorption and emission spectra of bulk solutions

In Fig. 2 the absorption and fluorescence emission spectra of PM, BPM and b_BPM in

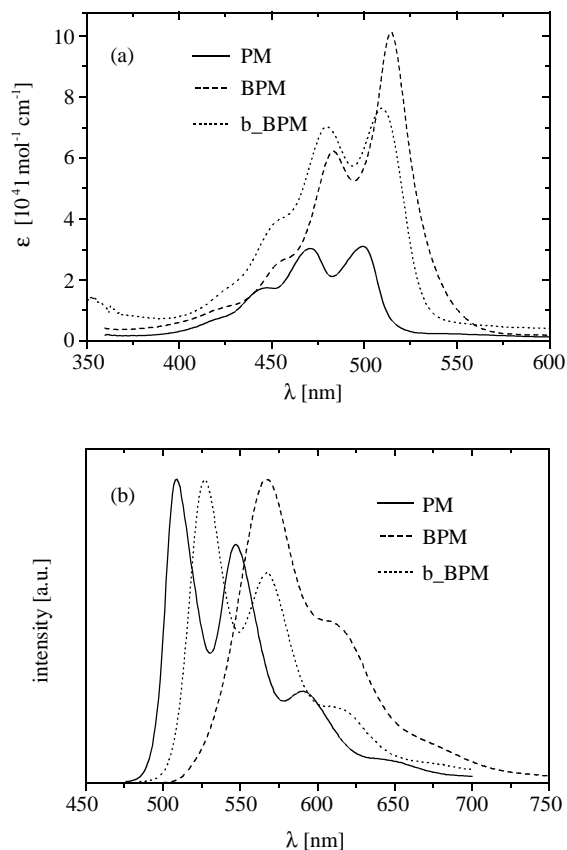


Fig. 2. (a) Absorption spectra of PM, BPM and b_BPM in tetradecane. The concentrations have been in the range of 3×10^{-6} mol/l; (b) fluorescence emission spectra of PM, BPM and b_BPM in tetradecane. The concentrations have been in the range of 5×10^{-7} mol/l.

tetradecane solution are shown. When comparing the absorption spectra of PM and BPM, clear differences are immediately visible. The long wavelength band of the BPM spectrum is shifted to the red (15 nm) and the overall spectral shape is largely altered. The most prominent feature is the strong absorption ($\epsilon \approx 100.000 \text{ l/mol cm}$) of the long wavelength absorption band. These differences between PM and BPM are attributed to inter-chromophore interactions in BPM. To qualitatively explain the observed effects, we refer to the exciton model applied by Kasha et al. to molecular dimers [2]. In this seminal paper, the authors introduced a quasi-classical vector model to describe the interaction of two transition dipoles under various geometries.

Recently, it has been reported that for a substituted bi-perylene, a dimer which is very similar to BPM, the dihedral angle between the two perylene moieties amounts to $\sim 70^\circ$ [18]. First electronic structure optimisations for BPM arrive at a slightly higher value. Therefore, both calculations indicate that the chromophores are almost orthogonal in the dimers, leading to negligible electronic orbital overlap. Based on these results and the reasonable assumption that the transition dipole in PM is oriented along the long molecular axis [19], BPM in a first approximation can be represented by the simple model shown in Fig. 3. The inclination angle θ between the transition dipole axes and the interconnecting line was estimated to be 9° assuming a distance r between the centres-of-mass of the two chromophores of 10 \AA . According to the exciton model [2] this configuration leads to an exciton band diagram as shown in Fig. 3. For a fixed distance between the transition dipoles, the strength of the splitting (ΔE) depends on the magnitude of the transition dipoles and the inclination angle θ . This relationship is expressed in the following equation [2]:

$$\Delta E = \frac{1}{4\pi\epsilon_0} \frac{2|M|^2}{r^3} (1 - 3\cos^2 \theta) \quad (1)$$

with M being the transition dipole. M has been obtained by integrating the absorption spectrum of the first electronic transition of PM ($M = 6.7 \text{ Debye}$) and applying standard expressions for the oscillator strength [20]. Inserting the

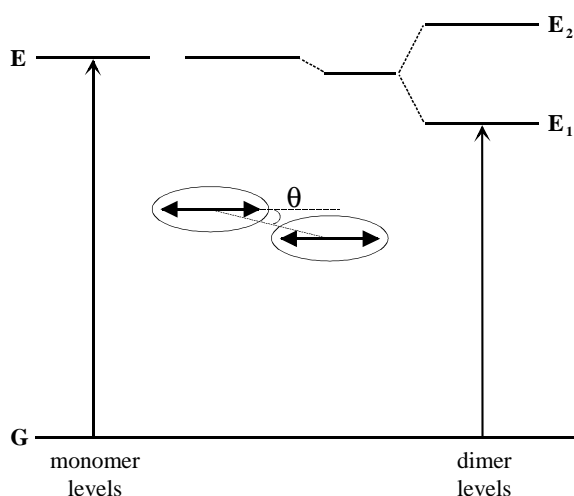


Fig. 3. Model for the excitonic splitting of BPM. The inset is a simple vector model for the interaction of the BPM transition dipoles which form an inclination angle θ with the axis connecting the dipoles. (for more details see text).

appropriate numbers into Eq. (1), we arrive at an exciton splitting $|\Delta E| = 870 \text{ cm}^{-1}$. This splitting is large enough to be easily observable even at room temperature.

For the geometry shown in Fig. 3 the exciton model [2] predicts that the red shifted transition is electric dipole allowed while the blue shifted transition is forbidden. These salient features of our simple approach can be qualitatively recovered in the absorption spectrum of BPM shown in Fig. 2(a). The long-wavelength transition is shifted to the red with respect to PM and carries a lot of oscillator strength. For a more quantitative comparison, besides the excitonic splitting, also the change in van-der Waals type dispersion interactions between the monomer and dimer has to be taken into account [2]. In Fig. 3 the latter contribution is depicted as a lowering of the excited state energy relative to a fixed ground state energy, although both states are influenced by a change in dispersion interactions. In the case of BPM in tetradecane what basically has to be considered is the difference of the dispersion interaction of PM in a tetradecane solvation shell and PM in a tetradecane solvation shell plus another PM in the solvation shell. This alteration

of the solvation shell should lead to energy lowering because of the high polarisability of π -electron systems. Along these lines, it is not surprising that the experimentally determined absorption red shift (585 cm^{-1}) is larger than half the calculated exciton splitting ($|\Delta E/2| = 435\text{ cm}^{-1}$). However, because our approach is very simple, the difference between these values should not be identified with the change in dispersion interaction energies.

In case of b_BPM the red shift of the absorption spectrum (as compared to PM) is smaller than for BPM. Additionally, the shape of the spectrum shows only minor differences to the PM absorption spectrum. Therefore, it seems reasonable to assume that the interaction strength is much weaker in the b_BPM dimer. When looking at the molecular structure of b_BPM, we have to take into account that this compound might exist in the “syn” and “anti” conformations. However, recent investigations of the parent benzil structure ($R\equiv H$ in Fig. 1) have indicated that benzil in various solvents exists in a single skewed conformation [21]. Preliminary electronic structure optimisations starting from the “syn” and “anti” conformations of b_BPM point to two skewed conformations which actually appear to be quite similar. For both conformations rough estimates have yielded exciton splittings in the range between 100 and 150 cm^{-1} . As these values are relatively small, we assume that the observed absorption red shift between PM and b_BPM ($\sim 430\text{ cm}^{-1}$) is mainly related to the interaction with the benzilic moiety in the dimer. A similar red shift has been observed for a single PM chromophore attached to a hexaphenylene unit where no inter-chromophore interactions can exist. Following these arguments, the dominating electronic interaction among the chromophores in the b_BPM dimer should be due to incoherent energy transfer of the Förster type. In both conformations the inter-chromophore distances ($\sim 15\text{--}20\text{ \AA}$) are well below the Förster radius of PM ($R_0 = 38\text{ \AA}$). This value of R_0 has been obtained by assuming random orientation between the chromophores [19].

The fluorescence spectra shown in Fig. 2(b) generally corroborate the conclusions drawn from the absorption spectra. When comparing the

vibronic structures of the emission spectra of the three compounds, it is seen that they are much more well resolved for PM and b_BPM. Additionally, BPM shows an exceptionally large Stokes shift which may be attributed to the higher polarisability of the delocalised excited state in BPM.

4. Single molecule experiments

To study the different behaviours of the monomer and the two dimers at the single molecule level, we have recorded fluorescence time traces and simultaneously measured emission spectra at 5 s time intervals, examples of which are shown in Figs. 4 and 5. In case of the PM monomer the time traces (not shown here) were similar for all 30 molecules investigated. After a period of constant emission intensity, the fluorescence signal dropped to the background level indicating an irreversible bleaching event. Reversible dark state transitions are only observed rarely for single PM molecules. The emission spectra of different PM molecules (not shown here) show variations in spectral position and relative band intensities [22]. This is a typical feature of single molecule investigations and mainly attributed to the inhomogeneous polymer environment or slight conformational differences between molecules. What is important to note in the present context is that for a given single PM molecule the spectra with the exception of small spectral shifts of a few nanometers basically did not change as a function of time until the final photobleaching occurred.

When single dimers are investigated, the fluorescence time traces as well as the emission spectra indicate a much more complex behaviour. In Figs. 4 and 5, fluorescence time traces and emission spectra of single BPM and b_BPM dimers, respectively, are collected. We first want to summarise the observations for BPM molecules which gave rise to different types of time traces. For the time trace shown in Fig. 4(a) the emission signal irreversibly ceased after 36 s. This kind of behaviour was found for 36% of the BPM molecules investigated and is called one-step signal drop. In Fig. 4(b) the emission signal changed in a

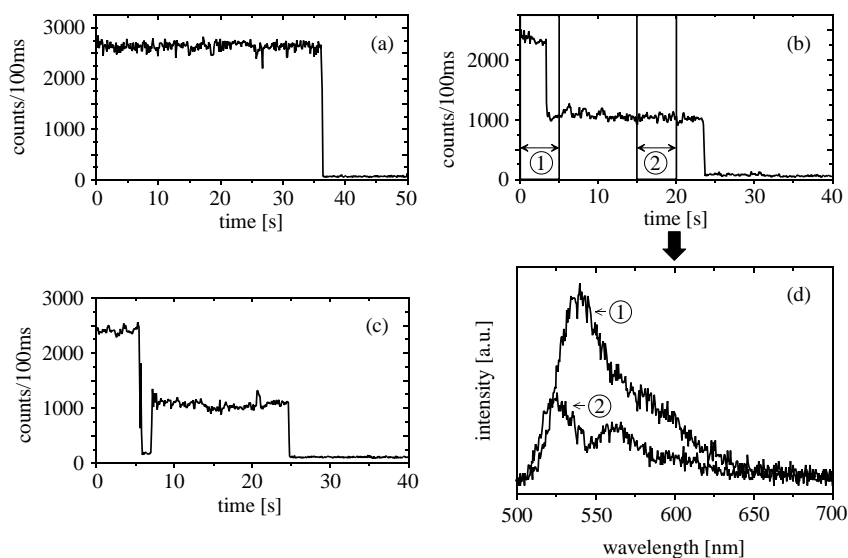


Fig. 4. Fluorescence intensity trajectories (time traces) for three single BPM molecules representing different types of intensity changes. (a) One-step signal drop; (b) two-step signal drop; (c) two-step signal drop including a reversible dark state; (d) fluorescence emission spectra recorded during the time intervals marked in (b). For all data shown in this figure the excitation intensity at 488 nm was set to 4.4 kW/cm^2 .

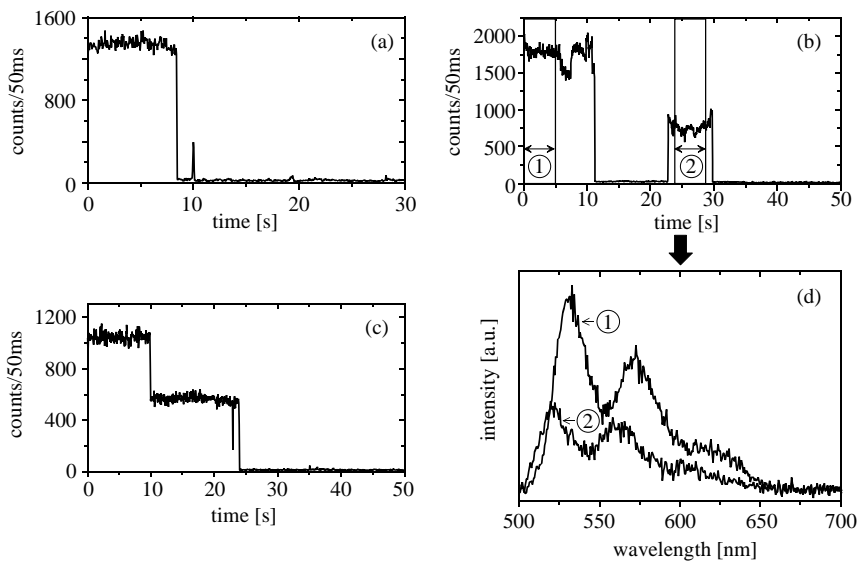


Fig. 5. Fluorescence intensity trajectories (time traces) for three single b.BPM molecules representing different types of intensity changes. (a) One-step signal drop; (b) two-step signal drop including a reversible dark state; (c) two-step signal drop; (d) fluorescence emission spectra recorded during the time intervals marked in (b). For all data shown in this figure the excitation intensity at 488 nm was set to 4.4 kW/cm^2 .

two-step sequential fashion until the final signal drop occurred (18% of molecules). Similar discrete step-wise changes were observed for the molecule whose data are shown in Fig. 4(c). In this case, however, the fluorescence signal first drops to the background level to emit at a different intensity level after residing in a dark state for several seconds. Such a two-step signal change including a reversible dark-state transition was found for 32% of the molecules investigated. For the remaining percentage of BPM molecules even more complex behaviour was found. In such cases the time traces showed multiple reversible dark-state transitions and sometimes more than two levels of emission intensity.

As was observed for PM, the emission spectra of different BPM dimers show variations in spectral position and relative band intensities. Since the main interest of the present study will focus on the discussion of spectral changes in relation to concomitant changes in the time traces for identical molecules, these distributions will not be considered further. Accordingly, a complete set of fluorescence spectra has been collected simultaneously with the time traces for every single dimer. During periods of constant emission intensity the spectra typically showed only slight spectral shifts as a function of time. However, spectral changes were observed whenever an intensity change was indicated by the time traces.

In Fig. 4(d) the fluorescence spectra of a single BPM molecule which have been recorded simultaneously with the time trace shown in Fig. 4(b) (two-step sequential signal drop) are displayed. The data indicate a blue shift of the spectrum after the first signal drop with a concomitant decrease of the overall spectral intensity. Another change relates to the vibrational structure of the spectra which became much more pronounced after the signal drop. For the BPM molecule the time trace of which is displayed in Fig. 4(c), the spectral changes (not shown here) were quite similar. The emission spectrum following the reversible dark state was blue shifted compared to the spectrum measured before the dark state and exhibited a more pronounced vibrational structure. The main difference to the previous case is the reversible dark state during which no emission is detectable.

By inspecting Fig. 5, it immediately becomes evident that the same typology of time traces as described for BPM was found for the b_BPM dimer. Besides one-step signal drops (16%), two-step sequential signal drops (28%) and two-step signal drops including a reversible dark-state transition (26%) were observed. As for BPM the remaining percentage of b_BPM molecules (30%) showed more complex behaviour with the same characteristics mentioned before. The spectral changes observed for b_BPM besides similarities to BPM also showed some remarkable differences. In Fig. 5(d), the emission spectra belonging to the time trace in Fig. 5(b) are displayed. The time trace was characterised by a two-step signal drop including a reversible dark-state transition. After the emission signal had reappeared, the spectrum had shifted to the blue. However, in contrast to the observations for BPM, the vibrational structure of the spectrum did only change to a very minor extent. The spectral changes recorded simultaneously with the time trace in Fig. 5(c) (not shown here) have been very similar to those just discussed.

5. Discussion

Qualitatively, similar observations as reported here have been obtained in single molecule investigations of other multichromophoric systems. Especially, the intriguing (reversible and/or irreversible) quenching of the total emission intensity seems to be a common feature of multichromophoric systems with interchromophore distances that allow for electronic interactions. Of particular interest for the present study are the single molecule experiments with dendrimers decorated at their rim with a variable number of PM monomers [15] and with the allophycocyanin (APC) trimer, a light harvesting protein complex [9].

We will start our discussion by considering the irreversible one-step signal drops which were observed for both dimers (Figs. 4 (a) and 5(a)). In accordance with previous investigations, the most likely explanation for this behaviour relates to the formation of a trap state which completely quenches the emission. It is reasonable to assume that this trap state is formed on a single monomer

site and then quenches the emission of the second intact monomer. Obviously, the quenching can occur over a range of distances because it is observed in BPM as well as in b.BPM which are characterised by different inter-chromophore distances. Long-range Förster type energy transfer seems to be a suitable mechanism for the observed quenching. As to the nature of the quenching state which appears to be non-fluorescent, we can only speculate at present. In accordance with other investigations of multichromophoric systems composed of organic dye molecules [7–9], a radical cation whose absorption spectrum overlaps the emission spectrum of intact PM would be a suitable candidate. While the absorption spectrum of the PM radical cation is not known, data are available for the perylene radical cation [23]. The absorption spectrum of the latter species in solution peaks at 546 nm. Assuming that the PM radical cation absorption would be in the same range (presumably shifted even more to the red), Förster transfer would be a possible scenario. Additionally, radical cations would not show up in the emission spectra because they are known to be non-fluorescent. Concerning the formation of a radical cation, it recently was argued in an investigation of single conjugated polymer molecules, that oxygen assists as an electron acceptor during the formation of a radical cation [24]. As our investigations have been performed in air, oxygen is abundant in the thin dimer-doped polymer films.

For the APC trimer studied by Ying et al. [9], it was suggested that emission from single pairs of strongly interacting chromophores is quenched by exciton trap formation within these pairs. This behaviour is very reminiscent of what is presented here in terms of a one-step signal drop. Radical cations which absorb but do not emit were identified as the most likely source for exciton traps. In the study of the aforementioned single conjugated polymer molecules [7,24] it was found that the emission from the polymer chain could be completely quenched by a single defect. Again, radical cations were suggested to act as efficient localised quenching sites. For a second-generation polyphenylene dendrimer carrying eight PM chromophores at the rim, collective on/off jumps of the

fluorescence intensity have been reported [15]. As a possible mechanism for the collective on/off jumps singlet–triplet energy transfer has been postulated. While such a mechanism can operate on the timescale of the triplet state lifetime, it certainly cannot explain dark states lasting many seconds or even much longer. Dark states in this time regime, which also have been observed for the dendrimer, again were tentatively interpreted to be caused by the formation of a radical cation/radical anion pair [15]. Following these results from the literature, the light-induced formation of radical cations seems to be a likely reason for fluorescence quenching in multichromophoric systems. However, in all investigations cited (including the present one), the independent spectroscopic proof for the presence of radical cations has not yet been achieved. An additional problem relates to the lifetime of those radicals which supposedly are highly reactive species. According to the data in Figs. 4(a) and 5(a) the lifetime has to be easily several tens of seconds. Therefore, the possibility for further reactions of these radicals cannot be excluded.

After the irreversible one-step signal drops we now want to examine the time traces which showed one or the other form of two-step behaviour. As a first example we want to discuss the observations for BPM as exemplified in Figs. 4(b) and (d). By comparing both figures it is seen that the emission spectrum had changed appreciably after the first signal drop. We attribute this behaviour to the loss of excitonic coupling within the dimer following a photochemical transformation of one of the chromophores. As long as both monomers are identical, they couple strongly and the emission originates from the lower excitonic level of the dimer (see Fig. 3) giving rise to the unstructured spectrum of BPM. After one of the chromophores has undergone a photochemical reaction, excitonic coupling is absent and the emission of the remaining intact PM is observed. In this context it is interesting to inspect the solution emission spectra of PM and BPM which are shown in Fig. 2. The BPM spectrum is appreciably red-shifted as compared to the PM spectrum and the latter shows a clearly resolved vibrational progression.

During the processes described before, BPM most probably is transformed into a dimer consisting of one intact PM molecule and a PM molecule which has undergone a photoreaction. Although the structure of the latter photoproduct is unknown, it is obvious that this specific photoproduct does not quench the emission of the remaining intact PM. Therefore, following the arguments from above it most probably cannot be a radical cation. Before discussing other possibilities, it is interesting to inspect the time trace given in Fig. 4(c). Here the two-step signal change is accompanied by a temporary dark state. As was mentioned before, the emission spectra before and after the dark state were almost identical to those shown in Fig. 4(d). Therefore, also for this type of behaviour the excitonic coupling seems to be destroyed by the formation of a photoproduct. In contrast to the previous case, however, this product is formed from a species which first quenches the emission of the dimer. This species could be again the much cited radical cation which would have to rearrange into a secondary product which has lost the spectral properties to quench the emission of the intact PM. Whether such rearrangements are possible is not known at present.

The data in Fig. 4(b) (supported by the spectra in (d)) would be compatible with the direct formation of a photoproduct being characterised by an absorption spectrum blue-shifted with regard to PM and negligible absorption at the fixed excitation wavelength of 488 nm. This would prevent Förster type quenching of the intact PM as well as observation of emission from the photoproduct. In a recent investigation of single terrylene molecules in a *p*-terphenyl crystal [25], it was demonstrated that reaction with singlet oxygen leads to a number of different photoproducts the main product being an exoperoxide whose absorption spectrum is blue shifted by 100 nm with respect to the parent compound. The formation of an exoperoxide cannot be ruled out in the present case, although there is no direct proof for such a scenario. From a more general point of view, at this point the question arises whether there is a distinct difference between the time traces shown in Figs. 4(b) and (c). It simply

could be that the dark period in a time trace like that in Fig. 4(b) is too short to be resolved within the experimental time resolution. If this would be true, both types of time traces have to be discussed on the same footing. Actually, the photooxidation studies of terrylene in *p*-terphenyl would also offer an explanation for the time trace in Fig. 4(c), because it was found that occasionally primary photooxidation products rearrange into secondary ones [25], the latter being characterised by an additional shift of the absorption spectrum. Summarising, at the present stage there is no real understanding of the photochemical processes which lead to the fluorescence intensity and spectral changes of the dimers. However, as will be seen in the following paragraphs the spectral consequences of the stepwise photochemistry allows for a distinction of strongly and weakly coupled dimers.

Phenomenologically, the single molecule time traces of b_BPM shown in Fig. 5 do not represent any fundamental difference to the data of BPM in Fig. 4. Actually, this observation is not too surprising, taking into account that the interchromophore distance in b_BPM is still in a regime where dipole–dipole energy-transfer processes are expected to function efficiently. Along these lines the irreversible and reversible dark states in Figs. 5(a) and (b), respectively, are thought to arise from the photoproducts tentatively proposed before, which quench the fluorescence emission of the remaining intact PM. The same arguments as used before may also equally apply to explain qualitatively the behaviour of b_BPM exemplified in Fig. 5(c). However, it is worthwhile noticing that the data for b_BPM lend additional support to the idea that the photochemistry occurs at only one of the chromophoric sites. In b_BPM the monomers are spatially well separated making it hard to imagine that a single photochemical reaction would transform both moieties at the same time.

A clear difference between BPM and b_BPM follows from the spectral changes (Figs. 4(d) and 5(d)) after one of the chromophores underwent a photoreaction. While the shape of the spectrum is appreciably modified in case of BPM (Fig. 4(d)), it is widely preserved for b_BPM. (The overall

intensity changes for both compounds are due to the weaker absorption of only one chromophore.) As was pointed out before, the electronic interactions in b.BPM are mainly attributed to incoherent excitation energy transfer. Taking into account that the inter-chromophore distance is much smaller than the Förster radius, it can be safely assumed that the rate of energy hopping is higher than the emission rate. Therefore, emission should occur with almost equal probability from both chromophoric sites, if their transition energies are nearly degenerate. If one of the chromophores has a lower transition energy, e.g. due to a different environment, emission should preferentially occur from this site. In any case the b.BPM dimer emission originates from a single chromophoric site, giving rise to an emission spectrum which closely resembles the PM spectrum. After one of the monomers has bleached no substantial change of the emission spectrum will occur. This is in contrast to BPM, where the loss of strong excitonic coupling leads to clear changes of the emission spectrum.

6. Conclusions and outlook

We have investigated two molecular dimers built from identical monomers which qualitatively represent the weak and strong coupling case with respect to their electronic interactions. Fluorescence intensity trajectories recorded at the single molecule level under ambient conditions showing one- or two-step intensity drops do not exhibit any substantial differences between both dimers. This at a first glance, surprising conformity probably originates from the same set of photochemical transformations supposed to occur at the monomer sites which are identical for both dimers. Substantial alterations, however, have been observed in the fluorescence emission spectra which for the strongly coupled dimer adopt a different shape after the excitonic splitting has been lifted through photochemistry of one of the monomers. By comparison of these results, it becomes obvious that the time traces, in general, might not contain sufficient information to distinguish weak and strong coupling between chromophores.

Following the foregoing discussion, it is mandatory to complement our investigations by measurement of more physical parameters. Polarisation modulation of the excitation beam and/or the emission light will give information on the orientation of the transition dipoles and concomitant changes after bleaching of one of the monomers. Along the same lines, correlation spectroscopy will report about changes in triplet lifetimes. One intriguing aspect concerns alterations of the intersystem crossing rate into the triplet state which is assumed to change when excitonic splitting vanishes [2]. By conducting experiments in an argon atmosphere, the influence of oxygen on the triplet kinetics and photochemistry can be elucidated. Finally, it is important to compare our results to larger multichromophoric systems. For a dendrimer carrying eight PM monomers at the rim, unstructured red-shifted emission spectra had been tentatively attributed to dimers [15]. The results presented here give first evidence as to which type of strongly coupled dimer gives rise to this type of spectra.

Acknowledgements

We would like to thank M. Haase and K. Pernigotto for experimental support. Financial support by the Volkswagen-Stiftung is gratefully acknowledged.

References

- [1] T. Förster, in: O. Sinanoglu (Ed.), *Modern Quantum Chemistry: Action of Light and Organic Crystals*, Academic Press, New York, 1965.
- [2] M. Kasha, H.R. Rawls, M. Ashraf Al-Bayoumi, *Pure Appl. Chem.* 11 (1965) 371.
- [3] E.E. Jelley, *Nature* 138 (1936) 1009.
- [4] G. Scheibe, *Angew. Chem.* 49 (1936) 563.
- [5] T. Förster, *Ann. Phys. (Leipzig)* 2 (1948) 55.
- [6] R.M. Clegg, in: X.F. Wang, B. Herman (Eds.), *Fluorescence Imaging Spectroscopy and Microscopy*, Wiley-Interscience, New York, 1996.
- [7] D.A. VandenBout, W.T. Yip, D.H. Hu, D.K. Fu, T.M. Swager, P.F. Barbara, *Science* 277 (1997) 1074.

- [8] M.A. Bopp, A. Syntik, T.D. Howard, R.J. Cogdell, R.M. Hochstrasser, *Proc. Natl. Acad. Sci. USA* 96 (1999) 11271.
- [9] L.M. Ying, X.S. Xie, *J. Phys. Chem. B* 102 (1998) 10399.
- [10] A.M. van Oijen, M. Ketelaars, J. Köhler, T.J. Aartsma, J. Schmidt, *Science* 285 (1999) 400.
- [11] C. Tietz, U. Gerken, F. Jelezko, J. Wrachtrup, *Single Mol.* 1 (2000) 67.
- [12] T. Ha, T. Enderle, D.S. Chemla, P.R. Selvin, S. Weiss, *Proc. Natl. Acad. Sci. USA* 93 (1996) 6264.
- [13] S. Weiss, *Science* 283 (1999) 1676.
- [14] T. Gensch, J. Hofkens, A. Herrmann, K. Tsuda, W. Verheijen, T. Vosch, T. Christ, Th. Basché, K. Müllen, F.C. De Schryver, *Angew. Chem. Int. Ed.* 38 (1999) 3752.
- [15] J. Hofkens, M. Maus, T. Gensch, T. Vosch, M. Cotlet, F. Köhn, A. Herrmann, K. Müllen, F.C. De Schryver, *J. Am. Chem. Soc.* 122 (2000) 9278.
- [16] H. Langhals, W. Jona, *Angew. Chem.* 110 (1998) 998.
- [17] F. Kulzer, F. Koberling, Th. Christ, A. Mews, Th. Basché, *Chem. Phys.* 247 (1999) 23.
- [18] M. Baumgarten, L. Gherghel, J. Firedrich, M. Jurczok, W. Rettig, *J. Phys. Chem. A* 104 (2000) 1130.
- [19] M. Maus, S. Mitra, M. Lor, J. Hofkens, T. Weil, A. Herrmann, K. Müllen, F.C. DeSchryver, *J. Phys. Chem. A* 105 (2001) 3961.
- [20] P.W. Atkins, R.S. Friedman, *Molecular Quantum Mechanics*, Oxford University Press, Oxford, 1997, p. 510.
- [21] Z. Pawelka, A. Koll, Th. Zeegers-Huyskens, *J. Mol. Struct.* 597 (2001) 57.
- [22] C. Blum, F. Stracke, S. Becker, K. Müllen, A.J. Meixner, *J. Phys. Chem. A* 105 (2001) 6983.
- [23] T. Shida, *Electronic Absorption Spectra of Radical Cations*, Elsevier, Amsterdam, 1988.
- [24] J. Yu, D. Hu, P.F. Barbara, *Science* 289 (2000) 1327.
- [25] Th. Christ, F. Kulzer, P. Bordat, Th. Basché, *Angew. Chem.* 113 (2001) 4327.